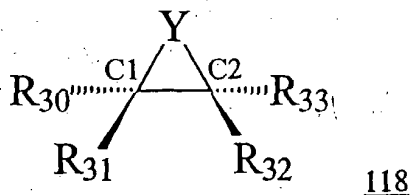


We Claim:

1. A process of stereoselective chemical synthesis, comprising: reacting a substoichiometric amount of a nucleophile with a racemic or diastereomeric mixture of a cyclic substrate, in the presence of a non-racemic, chiral catalyst, to effect a kinetic resolution of said cyclic substrate; said cyclic substrate comprises a carbocycle or heterocycle having an electrophilic center susceptible to attack by said nucleophile; and said chiral catalyst comprises an asymmetric tetradentate ligand complexed with a metal atom, which complex has a rectangular planar or rectangular pyramidal geometry.
2. The process of claim 1, wherein the metal atom is selected from Groups 3-12 of the periodic table, or from the lanthanide series.
3. The process of claim 1, wherein the metal atom is a transition metal from Groups 5-12.
4. The process of claim 1, wherein the metal atom is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru and Ni.
5. The process of claim 1, wherein the metal atom is Co.
6. The process of claim 1, wherein the tetradentate ligand is selected from the group consisting of: a chiral ligand represented by the formula 100; a chiral ligand represented by the formula 102; a chiral ligand represented by the formula 104; a chiral ligand represented by the formula 106; a chiral ligand represented by the formula 108; a chiral ligand represented by the formula 110; a chiral ligand represented by the formula 112; a chiral ligand represented by the formula 114; a chiral ligand represented by the formula 116; and a chiral crown ether.
7. The process of claim 1, wherein the tetradentate ligand comprises a Schiff base complexed with the metal atom.
8. The process of claim 1, wherein the chiral, non-racemic catalyst has a molecular weight of less than 5,000 a.m.u.
9. The process of claim 1, wherein the cyclic substrate is represented by the general formula 118:



wherein

Y represents O, S, N(R<sub>50</sub>), C(R<sub>52</sub>)(R<sub>54</sub>), or has the formula A-B-C; wherein R<sub>50</sub> is selected from the set comprising hydrogen, alkyls, acyls, carbonyl-substituted alkyls, carbonyl-substituted aryls, and sulfonyls; R<sub>52</sub> and R<sub>54</sub> each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C<sub>1</sub>-C<sub>5</sub> alkyl, O, S, carbonyl, or N(R<sub>50</sub>); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> represent organic or inorganic substituents which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

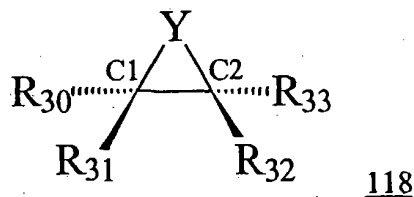
10. The process of claim 9, wherein the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>;

or any two or more of the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R<sub>7</sub> represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is an integer in the range of 0 to 8 inclusive.

11. The process of claim 1 or 9, wherein the cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.

12. The process of claim 1 or 9, wherein the cyclic substrate is a racemic or diastereomeric mixture of an epoxide, episulfide, or aziridine.

13. The process of claim 1, 2, 3, 4, or 5, wherein the cyclic substrate is a racemic terminal epoxide; and the nucleophile is water.
14. The process of claim 1, wherein the catalyst is immobilized on an insoluble matrix.
15. A process of stereoselective chemical synthesis, comprising: reacting a substoichiometric amount of a nucleophile with a racemic or diastereomeric mixture of a cyclic substrate, in the presence of a non-racemic, chiral catalyst, to effect a kinetic resolution of said cyclic substrate; said cyclic substrate comprises a carbocycle or heterocycle having an electrophilic center susceptible to attack by said nucleophile; and said chiral catalyst comprises an asymmetric tridentate ligand complexed with a metal atom, which complex has a trigonal planar or trigonal pyramidal geometry.
16. The process of claim 15, wherein the metal atom is selected from Groups 3-12 of the periodic table, or from the lanthanide series.
17. The process of claim 15, wherein the metal atom is a transition metal from Groups 5-12.
18. The process of claim 15, wherein the metal atom is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru and Ni.
19. The process of claim 15, wherein the metal atom is Co.
20. The process of claim 15, wherein the tridentate ligand comprises a Schiff base complexed with the metal atom.
21. The process of claim 15, wherein the chiral, non-racemic catalyst has a molecular weight of less than 5,000 a.m.u.
22. The process of claim 15, wherein the cyclic substrate is represented by the general formula 118:



wherein

Y represents O, S, N(R<sub>50</sub>), C(R<sub>52</sub>)(R<sub>54</sub>), or has the formula A-B-C; wherein R<sub>50</sub> is selected from the set comprising hydrogen, alkyls, acyls, carbonyl-substituted alkyls, carbonyl-substituted aryls, and sulfonyls; R<sub>52</sub> and R<sub>54</sub> each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C<sub>1</sub>-C<sub>5</sub> alkyl, O, S, carbonyl, or N(R<sub>50</sub>); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> represent organic or inorganic substituents which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

23. The process of claim 22, wherein the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or - (CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>;

or any two or more of the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R<sub>7</sub> represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is an integer in the range of 0 to 8 inclusive.

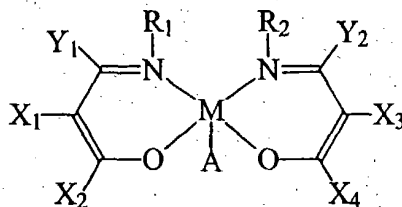
24. The process of claim 15 or 22, wherein the cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.

25. The process of claim 15 or 22, wherein the cyclic substrate is a racemic or diastereomeric mixture of an epoxide, episulfide, or aziridine.

26. The process of claim 15, 16, 17, 18, 19, or 22, wherein the cyclic substrate is a racemic terminal epoxide; and the nucleophile is water.

27. The process of claim 26, wherein the catalyst is immobilized on an insoluble matrix.

28. The process of claim 7, wherein the catalyst is represented by the general formula:



in which

the substituents  $R_1$ ,  $R_2$ ,  $Y_1$ ,  $Y_2$ ,  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  each, independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or  $-(CH_2)_m-R_7$ ,

or any two or more of the substituents taken together form a carbocycle or heterocycle ring having from 4 to 8 atoms in the ring structure,

with the proviso that at least one of  $R_1$ ,  $Y_1$ ,  $X_1$  and  $X_2$  is covalently bonded to at least one of  $R_2$ ,  $Y_2$ ,  $X_3$  and  $X_4$  to provide the b-iminocarbonyls to which they are attached as a tetradentate ligand, and at least one of  $Y_1$  and  $Y_2$  is a hydrogen;

$R_7$  represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

$m$  is an integer in the range of 0 to 8 inclusive;

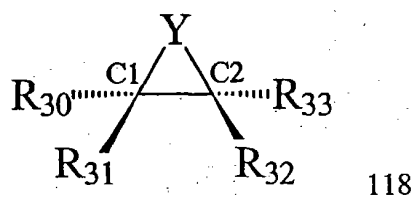
$M$  represents the metal atom; and

$A$  represents a counterion or a nucleophile,

wherein each of the substituents  $R_1$ ,  $R_2$ ,  $Y_1$ ,  $Y_2$ ,  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$ , are selected such that the catalyst is asymmetric.

29. The process of claim 28, wherein the metal atom is selected from Groups 3-12 of the periodic table, or from the lanthanide series.
30. The process of claim 28, wherein the metal atom is a transition metal from Groups 5-12.

31. The process of claim 28, wherein the metal atom is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru and Ni.
32. The process of claim 28, wherein the metal atom is Co.
33. The process of claim 28, wherein the chiral, non-racemic catalyst has a molecular weight of less than 5,000 a.m.u.
34. The process of claim 28, wherein the cyclic substrate is represented by the general formula 118:



wherein

Y represents O, S, N(R<sub>50</sub>), C(R<sub>52</sub>)(R<sub>54</sub>), or has the formula A-B-C; wherein R<sub>50</sub> is selected from the set comprising hydrogen, alkyls, acyls, carbonyl-substituted alkyls, carbonyl-substituted aryls, and sulfonyls; R<sub>52</sub> and R<sub>54</sub> each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C<sub>1</sub>-C<sub>5</sub> alkyl, O, S, carbonyl, or N(R<sub>50</sub>); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> represent organic or inorganic substituents which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

35. The process of claim 34, wherein the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or - (CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>;

or any two or more of the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R<sub>7</sub> represents

an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is an integer in the range of 0 to 8 inclusive.

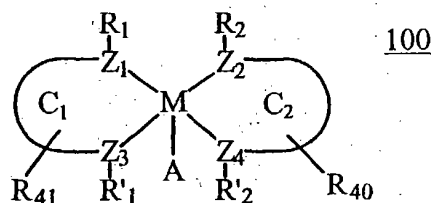
36. The process of claim 28 or 34, wherein the cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.

37. The process of claim 28 or 34, wherein the cyclic substrate is a racemic or diastereomeric mixture of an epoxide, episulfide, or aziridine.

38. The process of claim 28, 29, 30, 31, 32, or 34, wherein the cyclic substrate is a racemic terminal epoxide; and the nucleophile is water.

39. The process of claim 38, wherein the catalyst is immobilized on an insoluble matrix.

40. The method of claim 6, wherein the chiral catalyst is represented by general formula 100:



wherein

$Z_1$ ,  $Z_2$ ,  $Z_3$  and  $Z_4$  each represent a Lewis base;

the  $C_1$  moiety, taken with  $Z_1$ ,  $Z_3$  and  $M$ , and the  $C_2$  moiety, taken with  $Z_2$ ,  $Z_4$  and  $M$ , each, independently, form a heterocycle;

$R_1$ ,  $R_2$ ,  $R'_1$  and  $R'_2$  each, independently, are absent or represent a covalent substitution with an organic or inorganic substituent permitted by valence requirements of the electron donor atom to which it is attached;

$R_{40}$  and  $R_{41}$  each independently are absent, or represent one or more covalent substitutions of  $C_1$  and  $C_2$  with an organic or inorganic substituent permitted by valence requirements of the ring atom to which it is attached,

or any two or more of the  $R_1$ ,  $R_2$ ,  $R'_1$ ,  $R'_2$ ,  $R_{40}$  and  $R_{41}$  taken together form a bridging substituent;

with the proviso that  $C_1$  is substituted at at least one site by  $R_1$ ,  $R'_1$  or  $R_{41}$ , and  $C_2$  is substituted at at least one site by  $R_2$ ,  $R'_2$  or  $R_{40}$ , and

at least one of  $R_1$ ,  $R'_1$  and  $R_{41}$  taken together with at least one of  $R_2$ ,  $R'_2$  and  $R_{40}$  forms a bridging substituent so as to provide  $Z_1$ ,  $Z_2$ ,  $Z_3$  and  $Z_4$  as a tetradentate ligand;

M represents the metal atom; and

A represents a counterion or a nucleophile,

wherein each  $R_1$ ,  $R_2$ ,  $R'_1$ ,  $R'_2$ ,  $R_{40}$  and  $R_{41}$  are selected such that the tetradentate ligand is asymmetric.

41. The method of claim 40, wherein

$R_1$ ,  $R_2$ ,  $R'_1$  and  $R'_2$ , independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or  $-(CH_2)_m-R_7$ ;

each  $R_{40}$  and  $R_{41}$  occurring in 100 independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or  $-(CH_2)_m-R_7$ ;

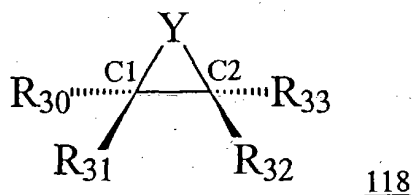
$R_7$  represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and

m is an integer in the range of 0 to 8 inclusive.

42. The method of claim 41, wherein each  $Z_1$ ,  $Z_2$ ,  $Z_3$  and  $Z_4$  are independently selected from the group consisting of nitrogen, oxygen, phosphorus, arsenic, and sulfur.



43. The process of claim 42, wherein the metal atom is selected from Groups 3-12 of the periodic table, or from the lanthanide series.
44. The process of claim 42, wherein the metal atom is a transition metal from Groups 5-12.
45. The process of claim 42, wherein the metal atom is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru and Ni.
46. The process of claim 42, wherein the metal atom is Co.
47. The process of claim 42, wherein the chiral, non-racemic catalyst has a molecular weight of less than 5,000 a.m.u.
48. The process of claim 42, wherein the cyclic substrate is represented by the general formula 118:



wherein

Y represents O, S, N(R<sub>50</sub>), C(R<sub>52</sub>)(R<sub>54</sub>), or has the formula A-B-C; wherein R<sub>50</sub> is selected from the set comprising hydrogen, alkyls, acyls, carbonyl-substituted alkyls, carbonyl-substituted aryls, and sulfonyls; R<sub>52</sub> and R<sub>54</sub> each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C<sub>1</sub>-C<sub>5</sub> alkyl, O, S, carbonyl, or N(R<sub>50</sub>); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> represent organic or inorganic substituents which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

49. The process of claim 48, wherein the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls,

or any two or more of the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R<sub>7</sub> represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is an integer in the range of 0 to 8 inclusive.

51. The process of claim 42 or 48, wherein the cyclic substrate is a racemic or diastereomeric mixture of an epoxide, episulfide, or aziridine.

53. The process of claim 52, wherein the catalyst is immobilized on an insoluble matrix.

wherein

the E<sub>1</sub> moiety, taken with Z<sub>1</sub>, Z<sub>2</sub> and M, and the E<sub>2</sub> moiety, taken with Z<sub>2</sub>, Z<sub>3</sub> and M, each, independently, form a heterocycle;

$R_{80}$  and  $R_{81}$  each independently are absent, hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or  $-(CH_2)_m-R_7$ , or any two or more of the  $R_{80}$  and  $R_{81}$  substituents taken together form a bridging substituent;

$R_7$  represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle;

$m$  is an integer in the range of 0 to 8 inclusive;

$M$  represents the metal atom; and

$A$  represents a counteranion or a nucleophile,

wherein the tridentate ligand is asymmetric.

55. The method of claim 54, wherein

$R_1$ ,  $R_2$ ,  $R'_1$  and  $R'_2$ , independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or  $-(CH_2)_m-R_7$ ;

each  $R_{40}$  and  $R_{41}$  occurring in 100 independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or  $-(CH_2)_m-R_7$ ;

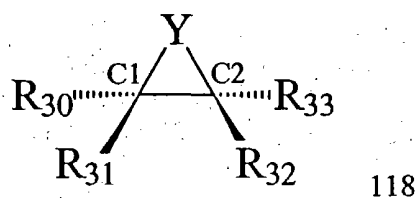
$R_7$  represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and

$m$  is an integer in the range of 0 to 8 inclusive.

56. The method of claim 55, wherein each  $Z_1$ ,  $Z_2$ ,  $Z_3$  and  $Z_4$  are independently selected from the group consisting of nitrogen, oxygen, phosphorus, arsenic, and sulfur.

57. The process of claim 56, wherein the metal atom is selected from Groups 3-12 of the periodic table, or from the lanthanide series.

58. The process of claim 56, wherein the metal atom is a transition metal from Groups 5-12.
59. The process of claim 56, wherein the metal atom is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru and Ni.
60. The process of claim 56, wherein the metal atom is Co.
61. The process of claim 56, wherein the chiral, non-racemic catalyst has a molecular weight of less than 5,000 a.m.u.
62. The process of claim 56, wherein the cyclic substrate is represented by the general formula 118:



wherein

Y represents O, S, N(R<sub>50</sub>), C(R<sub>52</sub>)(R<sub>54</sub>), or has the formula A-B-C; wherein R<sub>50</sub> is selected from the set comprising hydrogen, alkyls, acyls, carbonyl-substituted alkyls, carbonyl-substituted aryls, and sulfonyls; R<sub>52</sub> and R<sub>54</sub> each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C<sub>1</sub>-C<sub>5</sub> alkyl, O, S, carbonyl, or N(R<sub>50</sub>); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> represent organic or inorganic substituents which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

63. The process of claim 62, wherein the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or - (CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>;

or any two or more of the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R<sub>7</sub> represents

an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is an integer in the range of 0 to 8 inclusive.

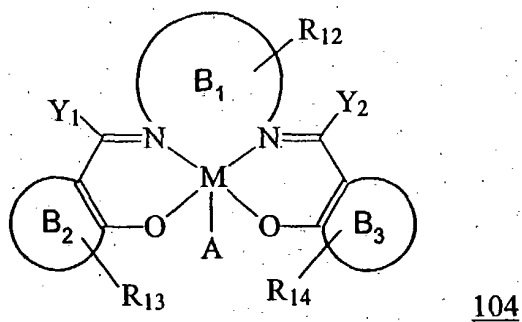
64. The process of claim 56 or 62, wherein the cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.

65. The process of claim 56 or 62, wherein the cyclic substrate is a racemic or diastereomeric mixture of an epoxide, episulfide, or aziridine.

66. The process of claim 56, 57, 58, 59, 60, or 62, wherein the cyclic substrate is a racemic terminal epoxide; and the nucleophile is water.

67. The process of claim 66, wherein the catalyst is immobilized on an insoluble matrix.

68. The method of claim 7, wherein the chiral catalyst comprising a chiral tetradentate ligand is represented by general formula 104:



wherein

the B<sub>1</sub> moiety represents a diimine bridging substituent represented by -R<sub>15</sub>-R<sub>16</sub>-R<sub>17</sub>, wherein R<sub>15</sub> and R<sub>17</sub> each independently are absent or represent an alkyl, an alkenyl, or an alkynyl, and R<sub>16</sub> is absent or represents an amine, an imine, an amide, a phosphoryl, a carbonyl, a silyl, an oxygen, a sulfur, a sulfonyl, a selenium, a carbonyl, or an ester;

each of B<sub>2</sub> and B<sub>3</sub> independently represent rings selected from a group consisting of cycloalkyls, cycloalkenyls, aryls, and heterocyclic rings, which rings comprising from 4 to 8 atoms in a ring structure;

Y<sub>1</sub> and Y<sub>2</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>;

R<sub>12</sub>, R<sub>13</sub>, and R<sub>14</sub> each, independently, are absent, or represent one or more covalent substitutions of B<sub>1</sub>, B<sub>2</sub> and B<sub>3</sub> with halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>, wherein R<sub>12</sub> can occur on one or more positions of -R<sub>15</sub>-R<sub>16</sub>-R<sub>17</sub>,

or any two or more of the R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, Y<sub>1</sub> and Y<sub>2</sub> taken together form a bridging substituent;

R<sub>7</sub> represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is an integer in the range of 0 to 8 inclusive;

M represents the metal atom; and

A represents a counterion or a nucleophile,

wherein R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, Y<sub>1</sub> and Y<sub>2</sub> are selected such that the catalyst is asymmetric.

69. The process of claim 68, wherein the metal atom is selected from Groups 3-12 of the periodic table, or from the lanthanide series.

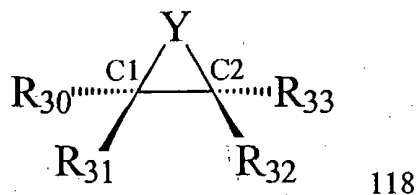
70. The process of claim 68, wherein the metal atom is a transition metal from Groups 5-12.

71. The process of claim 68, wherein the metal atom is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru and Ni.

72. The process of claim 68, wherein the metal atom is Co.

73. The process of claim 68, wherein the chiral, non-racemic catalyst has a molecular weight of less than 5,000 a.m.u.

74. The process of claim 68, wherein the cyclic substrate is represented by the general formula 118:



wherein

Y represents O, S, N(R<sub>50</sub>), C(R<sub>52</sub>)(R<sub>54</sub>), or has the formula A-B-C; wherein R<sub>50</sub> is selected from the set comprising hydrogen, alkyls, acyls, carbonyl-substituted alkyls, carbonyl-substituted aryls, and sulfonyls; R<sub>52</sub> and R<sub>54</sub> each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C<sub>1</sub>-C<sub>5</sub> alkyl, O, S, carbonyl, or N(R<sub>50</sub>); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

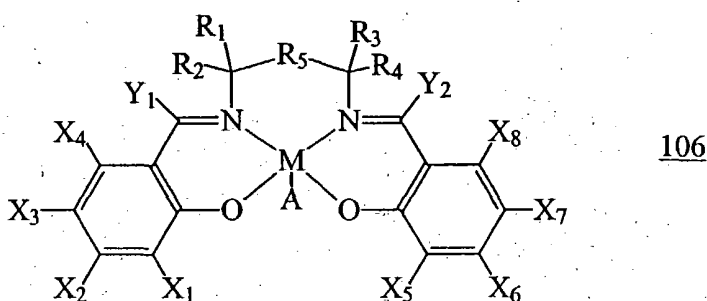
R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> represent organic or inorganic substituents which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

75. The process of claim 74, wherein the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>;

or any two or more of the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R<sub>7</sub> represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is an integer in the range of 0 to 8 inclusive.

76. The process of claim 68 or 74, wherein the cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.

77. The process of claim 68 or 74, wherein the cyclic substrate is a racemic or diastereomeric mixture of an epoxide, episulfide, or aziridine.
78. The process of claim 68, 69, 70, 71, 72, or 74, wherein the cyclic substrate is a racemic terminal epoxide; and the nucleophile is water.
79. The process of claim 78, wherein the catalyst is immobilized on an insoluble matrix.
80. The method of claim 7, wherein the metallosalenate catalyst is represented by general formula 106:



in which

each of the substituents  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $Y_1$ ,  $Y_2$ ,  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$ , independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or  $-(CH_2)_m-R_7$ ;

or any two or more of the substituents taken together form a carbocycle or heterocycle having from 4 to 10 atoms in the ring structure;

$R_7$  represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle;

$m$  is an integer in the range of 0 to 8 inclusive;

$M$  represents the metal atom; and

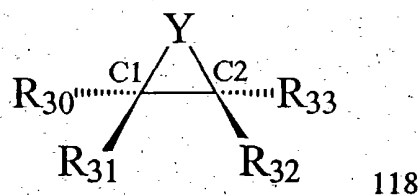
$A$  represents a counterion or a nucleophile;

wherein



if R<sub>5</sub> is absent, at least one of R<sub>1</sub> and R<sub>2</sub> is taken together with at least one of R<sub>3</sub> and R<sub>4</sub> to form a bridging substituent, and the substituents of 106 are selected such that the salenate is asymmetric.

81. The process of claim 80, wherein the metal atom is selected from Groups 3-12 of the periodic table, or from the lanthanide series.
82. The process of claim 80, wherein the metal atom is a transition metal from Groups 5-12.
83. The process of claim 80, wherein the metal atom is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru and Ni.
84. The process of claim 80, wherein the metal atom is Co.
85. The process of claim 80, wherein the chiral, non-racemic catalyst has a molecular weight of less than 5,000 a.m.u.
86. The process of claim 80, wherein the cyclic substrate is represented by the general formula 118:



wherein

Y represents O, S, N(R<sub>50</sub>), C(R<sub>52</sub>)(R<sub>54</sub>), or has the formula A-B-C; wherein R<sub>50</sub> is selected from the set comprising hydrogen, alkyls, acyls, carbonyl-substituted alkyls, carbonyl-substituted aryls, and sulfonyls; R<sub>52</sub> and R<sub>54</sub> each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C<sub>1</sub>-C<sub>5</sub> alkyl, O, S, carbonyl, or N(R<sub>50</sub>); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> represent organic or inorganic substituents which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

87. The process of claim 86, wherein the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or - (CH<sub>2</sub>)<sub>m</sub>-R<sub>7</sub>;

or any two or more of the substituents R<sub>30</sub>, R<sub>31</sub>, R<sub>32</sub>, and R<sub>33</sub> taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R<sub>7</sub> represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is an integer in the range of 0 to 8 inclusive.

88. The process of claim 80 or 86, wherein the cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.

89. The process of claim 80 or 86, wherein the cyclic substrate is a racemic or diastereomeric mixture of an epoxide, episulfide, or aziridine.

90. The process of claim 80, 81, 82, 83, 84, or 86, wherein the cyclic substrate is a racemic terminal epoxide; and the nucleophile is water.

91. The process of claim 90, wherein the catalyst is immobilized on an insoluble matrix.

92. The process of claim 1, 9, 15, 22, 28, 34, 42, 48, 56, 62, 68, 74, 80, or 86, wherein the nucleophile is water, an alcohol, or a thiol.

93. The process of claim 9, wherein the cyclic substrate is a racemic terminal epoxide; and the nucleophile is water.